Electronic conductivity of hydrogenated nanocrystalline silicon films

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A heteroquantum-dots (HQD) model for hydrogenated nanocrystalline silicon films (nc-Si:H) is proposed. The main features of our model are as follows. (i) the nanocrystalline grains and the amorphous counterparts in which they are embedded have very different band gap and band structures. As a result, they form heterojunctionlike structures in the interface regions, where the band offset effects dramatically reduce the activation energy and the grains act like quantum dots. (ii) In the presence of an external field, the activated electrons in the quantum dots conduct via quantum tunneling through the interface barriers. By means of the HQD model, we have identified the conduction of nc-Si:H as a thermal-assisted tunneling process. Our results show that there are two distinct regimes for the conductivity of nc-Si:H: (i) the low-temperature regime, where there is a simple activation energy ΔE; (ii) the high-temperature regime, where ΔE is effectively enhanced by the temperature effect of the electronic tunneling in the nanoscale particles. The theory is in good agreement with the experiments. © *1995 American Institute of Physics.*

I. INTRODUCTION

Recently, there has been extensive study of silicon systems, such as porous silicon[1,2] and c-Si/a-SiO_2 (nanoscale crystalline silicon particles embedded in amorphous silica),[3,4] where the nanoscale particles play an essential role. These materials have a common characteristic in that either the porous (for the porous silicon case) or the amorphous (for the c-Si/a-SiO_2 case) structure provides the means for a natural quantum confinement. (Note that in the case of artificial confinement[5,6] an external gate is used to produce the confinement.) Another interesting silicon system being extensively studied in the literature, the hydrogenated nanocrystalline silicon film (nc-Si:H),[7–15] also belongs to this kind of natural quantum confinement system. These nc-Si:H films are nanocrystalline materials,[16] and they are composed approximately of 50% nanocrystalline Si (mean grain size 3–5 nm) and 50% amorphous Si in the interface region (thickness about 2–3 atomic spacing).[11–14] Many interesting results have been reported which indicate that nc-Si:H films have very promising electronic and optical properties. It was found[12] that the room-temperature dc conductivity σ of nc-Si:H is in the range of 10^{-3}–10^{-1} $(\Omega\ \mathrm{cm})^{-1}$ (higher than that of the crystalliine Si) and the I–V curves of nc-Si:H films show some unusual nonlinear behavior.[14] Also,[9,12] the conduction is due to a peculiar thermal activation process, which has two different activation energies (0.10–0.15 eV below the room temperature and a dramatic increase above room temperature, as may be seen from a plot of the experimental data given in Fig. 2). Note that in the usual thermal activation situation, one has a single activation energy, which results in a negative slope in the semilog plot of σ vs $1/T$.

Previously, the grain-boundary-trapping (GBT) model, originally proposed for polycrystalline silicon (pc-Si), has been applied directly to explain the conductive properties of the nc-Si:H films.[8,9] According to the GBT model,[17,18] pc-Si is composed of small crystallites (size about 30 nm) joined together by a few disordered atomic layers (thickness about 1 nm), which results in carrier trapping at the grain boundary, creating a potential barrier. The conductance of pc-Si is also due to thermal activation and exhibits a negative temperature coefficient.[17,18] This latter fact prompts the direct application of the GBT model to the nc-Si:H films.[8,9] Nevertheless, the two main differences between the conductivity of pc-Si and nc-Si films, i.e., the different values of the activation energy (about 0.5 eV for pc-Si and 0.2 eV for nc-Si) and the distinct conductive features of two different activation energies in two different temperature regions for nc-Si films, remain unexplained by the GBT model.

In this article, we present the first attempt to develop a theoretical model, the heteroquantum dots (HQD) model, which explains the above-mentioned distinct transport features of the nc-Si:H films. The main ideas of the HQD model are:

(i) The nanocrystalline grains and their amorphous counterparts have very different band gap and band structures; as a result, they form heterojunctionlike structures in the interface regions, where the band offset effects dramatically reduce the activation energy and the grains act like quantum dots;

(ii) in the presence of an external field, the activated electrons in the quantum dots conduct via quantum tunneling through the interface barriers.

By means of the HQD model, we can identify the conduction of nc-Si:H as a thermal-assisted tunneling process: Electrons are first thermally activated to the quantum wells of the heterojunctions and then tunnel through the interface barrier. In order to apply the HQD model, we must first try to put the interface property of silicon nanocrystallite embedded in

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amorphous silicon (nc-Si/*a*-Si) in a more quantitative perspective, and then treat the electron tunneling in the network of nc-Si particles in detail. For these two fundamental problems, it is fortunate that there are many important advances in recent years. For the first problem there are two independent developments, i.e., the detailed study of the *c*-Si/*a*-Si heterostructure[19–21] and the insightful analysis of nc-Si particles embedded in a SiO_2 matrix.[3,4] As for the electron tunneling between the nanoscale particles, it is directly related to single electronics, a research field which has emerged in recent years.[22–26]

II. FORMULATION

We start by analyzing the interface property of silicon nanocrystallites embedded in amorphous silicon (nc-Si/*a*-Si) in terms of the important concepts of quantum dots (QD)[5,6] and heterostructures.[19–21] It is well known that QD are a two-dimensional electron gas (2DEG) which is confined by external gates laterally into equally distributed dots with diameters below 100 nm.[5,6] The nc-Si:H films are similar to QD in that the electrons are confined in the nanocrystalline grains. Nevertheless, there are major differences between QD and nc-Si:H in their constituent materials, size distribution of the dots, and electronic lateral transport. In QD the basic material of a 2DEG which forms the QD is homogeneous, the size of the dots is almost uniform, and lateral electronic transport is usually not possible due to the fact that a high barrier potential exists between the dots. As for nc-Si:H films, it is heterogeneous, i.e., there are two different materials, the *a*-Si in the interface regions and the nc-Si composing the grains with an unequally distributed size. Also, lateral electronic transport is possible in nc-Si:H films since the barrier potential is relatively low (thin interface region). Thus, it is reasonable to propose the HQD model, where the nanocrystalline grains and their amorphous counterpart in nc-Si:H form heterojunctionlike structures in the interface regions, due to their different band gaps and band structures. As a result, the band-offset effects dramatically reduce the activation energy and the grains act like QD with excess electrons. We now address the question of the detailed band-offset picture for the nc-Si/*a*-Si heterostructure, and what is the nanoscale effect.

The interface between *c*-Si and *a*-Si is a complex and interesting problem.[15,21] On the one hand, based on the notion that the presence of hydrogen in *a*-Si:H removes the top states of the valence band, it is speculated[15] that most of the offset is at the valence-band edge and the conduction band should line up quite well for the *c*-Si/*a*-Si heterojunction. On the other hand, there are many articles that deal directly with the problem of the band offset for the *a*-Si:H/*c*-Si heterostructures.[19–21] It is generally agreed that as long as there are enough Si—Si bonds at the *a*-Si side, the valence-band offset ΔE_v should be insignificant.[21] This view is strongly supported by the experimental data,[19–20] which also show that there is a strong conduction-band offset about 0.5 eV. Based on the above studies[19–21] we propose the following band picture for *a*-Si:H/*c*-Si heterostructure:

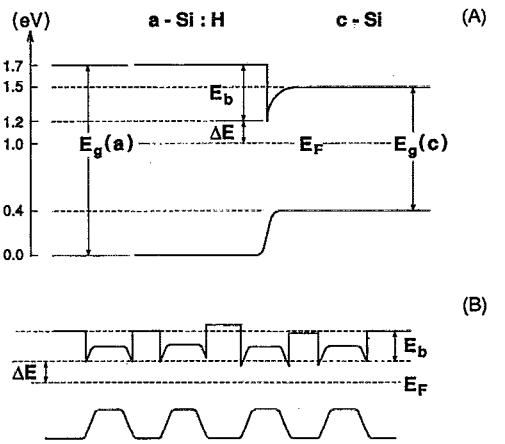

FIG. 1. Energy-band diagrams for (A) *a*-Si:H/*c*-Si heterojunction [the band gap of *c*-Si is $E_g(c)=1.1$ eV, the band gap of *a*-Si:H is $E_g(a)=1.7$ eV, the Fermi energy E_F is about 0.7 eV below $E_c(a)$, the barrier height E_b at the interface is about 0.5 eV, and the activation energy ΔE in the interface region is about 0.2 eV and (B) a network of *a*-Si:H/*c*-Si heterojunctions with various sized nanoscale *c*-Si particles.

(i) The Fermi energy E_F lies above the middle of the gap;
(ii) the conduction band E_c of *c*-Si is about 0.5 eV above E_F and that of *a*-Si is about 0.7 eV;
(iii) in the interface region, the conduction band of *c*-Si is only about 0.2 eV above E_F.

In Fig. 1(a) we further illustrate the energy diagram for *a*-Si:H/*c*-Si heterojunction, where we take the energy gap of *c*-Si as $E_g(c)=1.1$ eV, that of *a*-Si as $E_g(a)=1.7$ eV. Also, E_F is 0.7 eV below $E_c(a)$. The barrier height at the interface (i.e., the energy difference between the conduction band of *a*-Si and that of the interface) E_b is ~0.5 eV, and the activation energy in the interface region (i.e., the energy difference between the conduction band of *c*-Si at the interface and the Fermi level) ΔE is ~0.2 eV.

The actual structure for the nc-Si:H film is a network of *c*-Si/*a*-Si:H heterojunctions, with the relative components in the nanoscale. The main nanoscale effect on the band picture presented in Fig. 1(a) is that the energy gap $E_g(c)$ for *c*-Si will increase from its bulk value 1.1 eV due to the quantum confinement effects. As a result, as seen in Fig. 1(a), the conduction band of *c*-Si in nc-Si film is expected to move up from its corresponding bulk position. Thus, the actual value of E_b should be smaller than the bulk value (about 0.5 eV). It follows that the electrons in the nc-Si film have higher tunneling rates than those of the pc-Si film. In Fig. 1(b) we plot the energy diagram for a network of *a*-Si:H/*c*-Si heterostructures with various sizes of nanoscale *c*-Si particles. As can be seen from the figure that there is a fluctuation of band-edge energies in the system, which is caused by the size variations of the *c*-Si particles. We note that the HQD model proposed here is consistent with the model of the *c*-Si/*a*-SiO_2 system discussed recently by Tsu,[3] where electrons in the nanocrystalline Si embedded in the SiO_2 matrix are proposed as the trapped charges and located at the interface of *c*-Si/*a*-SiO_2.

We are now in a position to use the above-proposed HQD model to study the electronic conduction in the nc-Si:H

films in the presence of an external field. Basically, there are two main factors which contribute to the conductance of the nc-Si:H films: motion inside the dots and tunneling through the interface barriers. Since reducing the size to nanoscale will benefit all aspects of quantum confinement (such as reducing phonon scattering),[3] the transmitted electrons are essentially ballistic inside the dots. Thus, we will concentrate on studying how the electrons in the HQD conduct via tunneling through the interface barriers. According to the HQD model there exist activated electrons in the nc-Si particle which become the current carriers in the presence of an external field. It follows that in essence the electronic conduction in nc-Si:H films is a process of thermal-assisted tunneling, i.e., thermally activated electrons tunnel through the barrier. In the following we first analyze the thermal activation effects on the conduction, and then study the temperature dependence of the electron tunneling in a network of HQD.

For the thermal activation effect on the conduction, our HQD model follows closely the GBT model,[8,9] where the current carriers are thermally activated electrons in the interface regions between the a-Si and c-Si. The density of the activated electrons can be written as[9,15]

$$n=n_0 \exp(-\Delta E/k_BT), \tag{1}$$

where ΔE is the activation energy and n_0 is the electron density in the classical limit ($T\rightarrow\infty$). Using Eq. (1) one can evaluate the conductivity by means of the formula $\sigma=ne\mu$, where μ is the single electron mobility. According to the GBT model, the mobility μ is a temperature-independent quantity and the temperature behavior of the conductivity σ is therefore solely determined by Eq. (1). Apparently the GBT model does not include the temperature dependence of the electron tunneling in a network of HQD, which we discuss in the following.

The electron tunneling in a network of HQD is a complicated process, since each dot has different size and different environment. Here we adopt the simplest possible model where each dot has the same size, same environment, and same tunneling rate. In this case the problem reduces to the calculation of the tunneling of a single electron in a small junction, and one can use the known results from Refs. 22–26. For our purpose we need an expression for the single electron mobility μ, which can be obtained by directly using Eq. (15) of Ref. 25 as

$$\mu=\mu_0\int_{-\infty}^{\infty} dq\ P(q)\left[\frac{1}{1-e^{\beta\Delta E^+}}\left(1+\frac{\beta\Delta E^+}{e^{-\beta\Delta E^+}-1}\right)+\frac{1}{1-e^{\beta\Delta E^-}}\left(1+\frac{\beta\Delta E^-}{e^{-\beta\Delta E^-}-1}\right)\right]\equiv\mu_0 F(\langle q^2\rangle,T), \tag{2a}$$

where $\beta=1/k_BT$ and $P(q)$ is the charge distribution function, which takes care of the effects of the quantum charge fluctuation $\langle q^2\rangle$ on the dots. In addition, the change of the charging energy in Eq. (2a) due to the electron tunneling is given by

$$\Delta E^{\pm}=\left(1\pm\frac{2q}{e}\right)\frac{e^2}{2C}\equiv\left(1\pm\frac{2q}{e}\right)\epsilon_c. \tag{2b}$$

We note that the integral in Eq. (2a) represents the charging effects on the single electron tunneling. The value of the integral tends to one in the $T\rightarrow\infty$ limit, so that one identifies μ_0 as the classical mobility. Using Eqs. (1) and (2a), we obtain the conductivity for the nc-Si:H films,

$$\sigma=ne\mu=\sigma_0 \exp(-\Delta E/k_BT)F(\langle q^2\rangle,T), \tag{3}$$

where $\sigma_0=n_0e\mu_0$, and F is given by Eq. (2a).

Equation (3) is the main result of this article. It clearly shows that the conductivity of nc-Si:H has a complicated temperature behavior, i.e., it depends on both the activation process (the exponential factor) as well as the tunneling process (the function F). In the large charging energy limit ($\epsilon_c\gg k_BT$), the F of Eq. (2a) can be evaluated explicitly,[25] and it follows that Eq. (3) can be reduced to

$$\sigma=\sigma_0 \exp\left(\frac{-\Delta E}{k_BT}\right)\mathrm{erfc}\left(\frac{e}{\sqrt{8\langle q^2\rangle}}\right)\rightarrow\sigma_0\sqrt{\left(\frac{8\langle q^2\rangle^{1/2}}{\pi e^2}\right)}\exp\left(-\frac{\Delta E}{k_BT}-\frac{e^2}{8\langle q^2\rangle}\right), \tag{4}$$

where in the last step we have assumed $\langle q^2\rangle/e^2\ll 1$, and have used the asymptotic expression for the error function $\mathrm{erfc}(x)$. We note that in the literature[24,25] it is well known that $\langle q^2\rangle/e^2$ tends to a constant value, γ say, in the quantum ($T\rightarrow 0$) limit, and $\langle q^2\rangle/e^2=k_BT/2\epsilon_c$ in the classical limit ($k_BT\gg\hbar/CR_J$, with R_J the junction resistance). Based on these features of $\langle q^2\rangle$, from Eq. (4) one can immediately draw some qualitative conclusions for the conductivity σ:

(i) In the quantum limit $\langle q^2\rangle$ is not sensitive to T and $\sigma\sim e^{-\Delta E/k_BT}$;

(ii) in the classical limit $\langle q^2\rangle/e^2=k_BT/2\epsilon_c$ and $\sigma\sim\exp[-(\Delta E+\epsilon_c/4)/k_BT]$.

In principle $\langle q^2\rangle$ is related to the particular environment of the junction being studied, and can be evaluated by using the quantum Langevin equation.[24,25] With the above-mentioned properties in mind, here we use $\langle q^2\rangle$ as a parameter, and propose an empirical form,

$$\frac{\langle q^2\rangle}{e^2}=\frac{k_BT}{2\epsilon_c}\coth\left(\frac{k_BT}{2\gamma\epsilon_c}\right), \tag{5}$$

where γ is the value of $\langle q^2\rangle/e^2$ in the $T\rightarrow 0$ limit. We note that model (5) sets up a critical value of $2\gamma\epsilon_c=k_BT$, which separates the classical and quantum behavior for $\langle q^2\rangle$. Depending on the value of γ (which is related to the value of R_j; in general,[24,25] the larger the R_J the smaller the γ), Eq. (5) can exhibit either the quantum or the classic behavior in the region where $\epsilon_c\gg k_BT$. In summary, there is a striking difference between our model and the GBT model. In the latter model, the temperature dependence of σ is the same for all T whereas in our model the temperature dependence changes form as we go from low to high T (as will be clear from Fig. 2, discussed below) where the relevant curves have two distinct slopes.

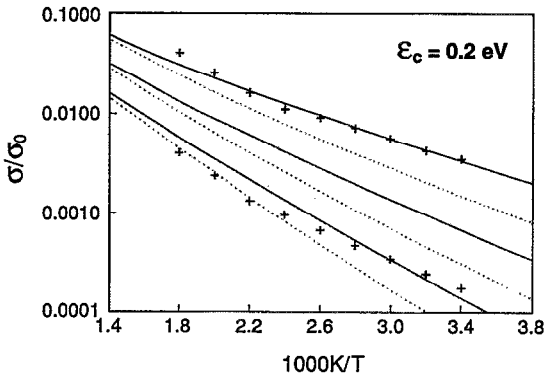

FIG. 2. Conductivity σ of nc-Si:H film (in units of its temperature independent part σ_0) vs 10^3 times the inverse of the temperature T (in units of K), at a charging energy ϵ_c=0.2 eV, for values of the charge fluctuating parameter γ=0.05 (dotted lines) and 0.1 (solid lines), and three different values (from top to bottom) of activation energy $\Delta E/\epsilon_c$=0.5, 0.7, 0.9, calculated by Eqs. (4) and (5) of the HQD model. Symbols are experimental data taken from Ref. 12.

Using Eqs. (4) and (5), we now study in detail the conductivity of nc-Si:H films as a function of γ, ΔE, and ϵ_c. A typical example is illustrated in Fig. 2, where we have plotted (semilogarithmic) the conductivity σ/σ_0 vs the inverse of temperature at ϵ_c=0.2 eV, γ=0.05, 0.1, and $\Delta E/\epsilon_c$=0.5, 0.7, 0.9. As can be seen from the figure, in general σ/σ_0 increases with increasing γ and with decreasing $\Delta E/\epsilon_c$. Also, the rate of increase of the σ/σ_0 is faster in the high-temperature region ($2\gamma\epsilon_c < k_BT$) than in the low-temperature region ($2\gamma\epsilon_c > k_BT$). In the low-temperature limit the slope tends to ΔE, while in the high-temperature limit the slope tends to $\Delta E + \epsilon_c/4$. For comparison, in Fig. 2 we have also plotted the experimental data of the conductivity for the nc-Si:H films taken from Ref. 12. As can be seen from the figure, the fitting between the experimental data and our theoretical predictions is reasonably good. We note that the realistic values for some key quantities appeared in our theory, viz., the junction capacitance C, the charging energy $\epsilon_c = e^2/2C$, and the activation energy ΔE, can be estimated as follows. From the experimental data[11–14] the size of the nanoscale c-Si particles is around 3 nm, from which we estimate the junction capacitance $C \sim 10^{-19}$ F. It follows that the corresponding charging energy is ϵ_c in the range of 0.1–0.2 eV. Also, the activation energy at low temperature ($k_BT \ll \epsilon_c$) is estimated as $\Delta E \sim 0.1$–0.3 eV. These values fall closely in the region where we perform our theoretical calculations as shown in Fig. 2.

III. CONCLUSION

In this article we have proposed a HQD model for nc-Si:H films which identifies the conduction of nc-Si:H as a thermal-assisted tunneling process. In this HQD model the nanocrystalline grains and their amorphous counterparts have very different band gap and band structures, and they form heterojunctionlike structures in the interface regions, where the band-offset effects dramatically reduce the activation energy. This explains why the activation energy of nc-Si films is much lower than that of the pc-Si. Also, the HQD model indicates that in the presence of an external field the activated electrons in the quantum dots conduct via quantum tunneling through the interface barriers. This tunneling process gives an extra temperature dependence to the conductivity of nc-Si:H films, and gives rise to the two different activation energies in two different temperature regions. Our detailed results show that the two distinct regimes for the conductivity of nc-Si:H are:

(i) the low-T regime, where there is a simple activation energy ΔE;
(ii) the high-T regime, where the activation energy ΔE is effectively enhanced by the order of ϵ_c due to the temperature effect of the electronic tunneling.

The theory is in good agreement with the experiments.

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